Design, synthesis and study of mechanical behaviour of tough hydrophobically associated, metal-ligand based hydrogels and their multifunctional applications

ABSTRACT

Polymer hydrogels consist of three-dimensional polymeric network which has a great potential to be used in a wide range of applications such as tissue engineering, actuator, sensor, OLED, drug delivery etc. However, for the conventional hydrogels, the poor mechanical properties as well as inefficient self-recovery after the application of load limit the scope of applications. In this work, a dual physical cross-linking strategy (hydrophobic association and metal-ligand cross-links) has been employed to access hydrogel materials with good mechanical strength, toughness and anti-fatigue characteristics. Using micellar copolymerization method, acrylamide and a hydrophobic acrylic monomer (containing a terpyridine ligand to provide metal-ligand interaction) were copolymerized to obtain polymer hydrogels in the presence of different metal ions (M^{2+}). The strong Fe^{2+}-terpy cross-links enhanced the mechanical properties of the hydrogels whilst the weaker and kinetically labile Zn^{2+}-terpy coordination produced hydrogels with lower mechanical properties and self-healing ability. This copolymerization system was then modified by (a) adding methacrylic acid (MA) as a monomer (to enhance mechanical properties) and (b) introducing lanthanide ions (Ln^{3+}) for cross-linking with the hydrophobic terpyridine ligand. The Ln^{3+}-terpyridine cross-links acted as a sacrificial motif to dissipate energy and also as a sensitizer for the lanthanide ions to provide higher metal centred luminescence. This luminescent hydrogel showed excellent tensile and compressive recovery properties after loading-unloading cycles. Applications as a flexible resistive and emissive strain sensor as well as fluorescent anticounterfeiting ink were demonstrated. To achieve high tensile strength (in MPa range) in this class of hydrogel materials, the hydrogels were synthesized in the absence of metal ions. After pre-stretching (at various strain% such as 100%, 200% and 300%) and air drying, the metal (Fe^{3+})-terpyridine and metal-carboxylate cross-links were established, locking the orientation of the polymer chains. The mechanical properties were significantly enhanced in the pre-stretching direction (mechanical strength of 1.6 - 2.7 MPa, toughness of 3 - 4 MJ m^{-3} and elastic modulus of 1.7 - 2.5 MPa). The application of the hydrogel as anisotropic resistive sensor and anisotropic bilayer actuator were explored.

Key words: Metal-ligand cross-links, hydrophobic association, photoluminescent hydrogel, stimuli-responsive, anisotropic hydrogel, self-recovery, self-healing.